OPTICAL AND TERAHERTZ RESPONSE OF CARBON NANOSTRUCTURES: QUANTUM DOTS, NANOTUBES AND GRAPHENE

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by

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Submitted

in fulfillment of the requirement of the degree of Doctor of Philosophy

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DEDICATED

to

My Parents and Teachers

CERTIFICATE

This is to certify that the thesis entitled, **"Optical and Terahertz Response of Carbon Nanostructures: Quantum Dots, Nanotubes and Graphene"**, being submitted by **Mr. Arvind Singh** to the Department of Physics, Indian Institute of Technology Delhi, New Delhi, for the award of degree of **Doctor of Philosophy** in Physics is a record of bona fide research work carried out by him under my supervision and guidance. He has fulfilled the requirements for submission of the thesis, which to the best of my knowledge has reached the requisite standard.

The material contained in the thesis has not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

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ARVIND SINGH

Abstract

Carbon, as the main building block of organic compounds, is one of the most important chemical elements essential for all living organisms. Much of the discussion on nanotechnology perspectives has been centered around carbon-based nanostructures in the last three decades due to the popularity of fullerenes, nanotubes, and unprecedented success of graphene. The interest in low-dimensional carbon materials has been exponentially growing ever since, because of their exceptional electrical, chemical, thermal, and optical properties. Carbon-based nanomaterials, in particular, carbon nanotubes (CNTs) and graphene, provide a variety of new opportunities for fundamental and applied research across many disciplines of science. A prerequisite for many of these applications is a thorough understanding of the nature of the elementary and coupled excitations, and various dynamical processes involving them. There are three facets of the work that has been conducted for the current thesis. The first one deals with the study of the electrical and linear optical properties including light-emitting characteristics of suspensions and thin films of carbon quantum dots and nanoparticles. Starting from graphitic microparticles, the carbon quantum dots and nanoparticles were synthesized by nanosecond laser ablation in ultrastable aqueous suspensions and thin films, respectively. The reason for the ultrastability of the quantum dot suspensions without the use of any additives/surfactants was determined to be due to the similar charges developed on them during the growth itself. Electrical measurements on thin films of carbon nanoparticles revealed a hopping mechanism for electrical conduction. Simultaneous measurements confirmed persistent photoconductivity which implies the presence of a large density of localized/disordered states. Other than oxygenated impurities that are responsible for the luminescent properties of the amorphous carbon nanoparticle films, clear signatures of shallow and deep level localized or trap states were determined from the temperature-dependent electrical and optical experiments. The second part of the work involved extensive use of femtosecond laser pulses for the determination of hot carrier dynamics in carbon nanotubes and graphene oxide flakes. Femtosecond time-resolved optical pump-probe spectroscopy of single walled carbon nanotubes (SWCNTs) helped us to determine

electron-phonon coupling strength and π-plasmon dynamics in them. Competing photobleaching and induced-absorption effects, involving processes of intraband relaxation and intertube coupling in bundles by charge transfer, were observed simultaneously within the first 200 fs in the recovery of the photoinduced changes in the ultrafast response. Ultrafast photoresponse through time-resolved differential transmission measurements revealed three relaxation channels for carrier/energy decay in graphene oxide flakes. The first two time-constants of the decay process are same as the signature features of pristine graphene, however, a third and much weaker component with time-constant of ~70 ps is also observed, which has to do with the defects and oxygenated impurities in graphene oxide. Detailed temperature-dependent measurements allowed us to understand the phonon bottleneck behavior in the hot carrier relaxation dynamics. In the last part of the thesis, sub-bandgap photoactivation in a transition dichalcogenide monolayer sandwiched between two graphene layers has been studied by employing ultrashort THz pulses. For these measurements, sub-picosecond THz pulses were generated by dual-colour ultrafast air-plasma to employ them as probe pulses for measuring femtosecond optical pulses-induced effects in the specially designed tri-layer heterostructure. The photogenerated carrier gradient in the two graphene layers, separated by the transition metal dichalcogenide layer provides the main force for the carriers to migrate to the intermediate layer facilitating enhancement in the overall photocarrier generation and hence optical pump-induced THz response from the system as compared to either graphene or the transition metal dichalcogenide monolayer alone. Besides, the stationary THz conductivity in an ultrabroad THz frequency range has also been measured for the individual layers as well as the heterostructures, which is a very good addition to the literature for determining futuristic applications of such quantum materials for all-optical devices.

सारांश

कार्बन, कार्बनिक यौगिकों के मुख्य निर्माण खंड के रूप में, सभी जीवित जीवों के लिए आवश्यक सबसे महत्वपूर्ण रासायनिक तत्वों में से एक है। फुलरीन, नैनोट्यूब की लोकप्रियता और ग्रेफीन की अभूतपूर्व सफलता के कारण पिछले तीन दशकों में नैनो-प्रौद्योगिकी के दृष्टिकोण पर अधिकांश चर्चा कार्बन-आधारित नैनोस्ट्रक्चर के आसपास केंद्रित रही है। उनके असाधारण विद्युत, रासायनिक, थर्मल और ऑप्टिकल गुणों के कारण, निम्न-आयामी कार्बन सामग्री में रुचि तेजी से बढ़ रही है। कार्बन आधारित नैनोमैटेरियल्स, विशेष रूप से, कार्बन नैनोट्यूब (सीएनटी) और ग्रैफेन, विज्ञान के कई विषयों में मौलिक और अनुप्रयुक्त अनुसंधान के लिए कई नए अवसर प्रदान करते हैं। इनमें से कई अनुप्रयोगों के लिए एक शर्त प्राथमिक और युग्मित उत्तेजनाओं की प्रकृति और उन्हें शामिल करने वाली विभिन्न गतिशील प्रक्रियाओं की गहन समझ है। वर्तमान थीसिस के लिए किए गए कार्य के तीन पहलू हैं। पहला, कार्बन क्वांटम डॉट्स और नैनोकणों की निलंबन और पतली फिल्मों की प्रकाश उत्सर्जक विशेषताओं सहित विद्युत और रैखिक ऑप्टिकल गुणों के अध्ययन से संबंधित है। ग्रेफाइटिक माइक्रोपार्टिकल्स से शुरू होकर, कार्बन क्वांटम डॉट्स और नैनोकणों को क्रमशः अल्ट्रास्टेबल जलीय निलंबन और पतली फिल्मों में नैनोसेकंड लेजर एब्लेशन द्वारा संश्लेषित किया गया था। किसी भी एडिटिव्स/सर्फैक्टेंट्स के उपयोग के बिना क्वांटम डॉट सस्पेंशन की अल्ट्रास्टेबिलिटी का कारण विकास के दौरान ही उन पर विकसित समान चार्ज के कारण निर्धारित किया गया था। कार्बन नैनोकणों की पतली फिल्मों पर विद्युत मापन ने विद्युत चालन के लिए एक हॉपिंग तंत्र का खुलासा किया। एक साथ मापन ने लगातार फोटोकॉन्डक्टिविटी की पुष्टि की जिसका तात्पर्य स्थानीयकृत / अव्यवस्थित राज्यों के बड़े घनत्व की उपस्थिति से है। ऑक्सीजन युक्त अशुद्धियों के अलावा, जो अनाकार कार्बन नैनोपार्टिकल फिल्मों के ल्यूमिनसेंट गुणों के लिए जिम्मेदार हैं, उथले और गहरे स्तर के स्थानीयकृत या जाल राज्यों के स्पष्ट हस्ताक्षर तापमान-निर्भर विद्युत और ऑप्टिकल प्रयोगों से निर्धारित किए गए थे। काम के दूसरे भाग में कार्बन नैनोट्यूब और ग्रैफेन ऑक्साइड फ्लेक्स में गर्म वाहक गतिशीलता के निर्धारण के लिए फेमटोसेकंड लेजर दालों का व्यापक उपयोग शामिल था। एकल दीवार वाले कार्बन नैनोट्यूब (एसडब्ल्यूसीएनटी) के फेमटोसेकंड समय-समाधान ऑप्टिकल पंप-जांच स्पेक्ट्रोस्कोपी ने हमें इलेक्ट्रॉन-फोनन युग्मन शक्ति और उनमें π-प्लास्मोन गतिशीलता निर्धारित करने में मदद की। फोटोब्लीचिंग और प्रेरित-अवशोषण प्रभावों का मुकाबला, चार्ज ट्रांसफर द्वारा बंडलों में इंट्राबैंड छूट और इंटरट्यूब कपलिंग की प्रक्रियाओं को शामिल करते हुए, अल्ट्राफास्ट प्रतिक्रिया में फोटोइंड्रेटेड परिवर्तनों की वसूली में पहले 200 एफएस के भीतर एक साथ देखा गया था। समय-समाधान अंतर संचरण माप के माध्यम से अल्ट्राफास्ट फोटोरस्पॉन्स ने ग्राफीन ऑक्साइड फ्लेक्स में वाहक / ऊर्जा क्षय के लिए तीन विश्राम चैनलों का खुलासा किया। क्षय प्रक्रिया के पहले दो समय-स्थिरांक प्राचीन ग्रैफेन की हस्ताक्षर विशेषताओं के समान हैं, हालांकि, $\sim$ 70 पीएस के समय-स्थिरांक के साथ एक तीसरा और बहुत कमजोर घटक भी देखा जाता है, जिसका दोष और ऑक्सीजन युक्त अशुद्धियों से संबंधित है ग्राफीन ऑक्साइड में विस्तृत तापमान-निर्भर माप ने हमें गर्म वाहक विश्राम गतिकी में फोनन टोंटी के व्यवहार को समझने की अनुमति दी। थीसिस के अंतिम भाग में, अल्ट्राशॉर्ट THz दालों को नियोजित करके दो ग्राफीन परतों के बीच सैंडविच किए गए एक संक्रमण डाइक्लोजेनाइड मोनोलेयर में उप-बैंडगैप फोटोएक्टीवेशन का अध्ययन किया गया है। इन मापों के लिए, उप-पिकोसेकंड THz दालों को दोहरे रंग के अल्ट्राफास्ट एयर-प्लाज्मा द्वारा उत्पन्न किया गया था ताकि उन्हें विशेष रूप

से डिज़ाइन किए गए ट्राई-लेयर हेटरोस्ट्रक्चर में फेमटोसेकंड ऑप्टिकल पल्स-प्रेरित प्रभावों को मापने के लिए जांच दालों के रूप में नियोजित किया जा सके। दो ग्राफीन परतों में फोटोजेनरेटेड वाहक ढाल, संक्रमण धातु डाइक्लोजेनाइड परत द्वारा अलग किया गया, वाहकों को समग्र फोटोकैरियर पीढ़ी में वृद्धि की सुविधा के लिए मध्यवर्ती परत की ओर पलायन करने के लिए मुख्य बल प्रदान करता है और इसलिए सिस्टम से ऑप्टिकल पंप-प्रेरित THz प्रतिक्रिया की तुलना में अकेले ग्राफीन या संक्रमण धातु डाइक्लोजेनाइड मोनोलेयर के लिए। इसके अलावा, एक अल्ट्राब्रॉड THz फ्रीक्वेंसी रेंज में स्थिर THz चालकता को व्यक्तिगत परतों के साथ-साथ हेटरोस्ट्रक्चर के लिए भी मापा गया है, जो कि सभी-ऑप्टिकल उपकरणों के लिए ऐसी क्वांटम सामग्री के भविष्य के अनुप्रयोगों को निर्धारित करने के लिए साहित्य के लिए एक बहुत अच्छा अतिरिक्त है।

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